

# Supporting Information

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## SI Text

**Controversy Background Information.** Large-scale commercial oil sands mining near the Athabasca River began in the late 1960s (1), approximately 250 km upstream of the northern Alberta community of Fort Chipewyan. Residents have since reported long-term declines in the populations of many fish and wildlife species and in the quality of water and fish obtained from the river, its delta and Lake Athabasca (2, 3), part of lands guaranteed to indigenous inhabitants by Canada under Treaty 8 of 1899.

Concerns about the health of residents emerged well over a decade ago with recommendations in the 1990s for ongoing monitoring of environmental and human health throughout the northern river basins [Northern River Basins Study (4)]. A companion study, on the health of Albertans residing in the Peace and Athabasca River basins, specifically recommended inclusion of Fort Chipewyan's Nunee Health Authority in environmental health studies because of "their unique interest in environmental contaminants resulting from their geographic location and consumption of foods from local sources" (5). Recommended monitoring included measuring fish, wildlife, human exposure, and human health outcomes related to local contaminants of concern (4, 5).

In 2006, local physician Dr. John O'Connor reported an unusual incidence of rare cancers, thyroid problems, and other diseases related to immune impairment in Fort Chipewyan (3, 6). A subsequent study suggested that cancer rates in Fort Chipewyan were comparable with Alberta provincial averages, although the incidence of hypertension, renal failure, diabetes, and lupus was elevated (7). However, a more recent detailed study indicated that the overall cancer rate and incidence of blood and lymphatic system cancers, grouped biliary tract cancers, and soft tissue cancers in Fort Chipewyan were higher than expected (8). Residents attribute increased cancer rates to environmental contamination from industrial sources, including oil sands development (3, 8). The degree to which oil sands development contributes to chemical contaminants in the Athabasca River and its tributaries, and to the health of people in the region, remains highly controversial.

Oil sands contain a broad array of the chemicals typical of petroleum, including three- to five-ringed polycyclic aromatic hydrocarbons (PAHs) and a variety of trace metals (9–11). Many of these constituents are highly toxic, some are carcinogenic, and all can be distributed widely via gases and dust originating from oil sand mining and processing. These facilities and in situ operations can also affect nearby water bodies via land clearing, excessive water withdrawals, pipeline and road crossings that increase erosion and sedimentation rates, release and deposition of airborne pollutants, and spills or leaks from operations or tailings ponds (6).

Contaminant releases to the Athabasca River have been documented. In June 1970, an oil pipeline leak to the Athabasca River disrupted the drinking water supply of Fort MacKay and Fort Chipewyan and commercial fishing on Lake Athabasca (12). A winter tailings spill under ice in 1981–82 contaminated a large downstream section of the Athabasca River with PAHs, dibenzothiophenes, phenolics, and other contaminants (13).

One difficulty with assessing time trends in many of the contaminants in the Athabasca River is that many of the sensitive analytical methods in use today were not available in the early years of oil sands mining. Also, as rapid development has proceeded, there are few remaining pristine catchments that can serve as reference watersheds within the area where mining is possible.

In 2003, the Northern Rivers Ecosystem Initiative concluded that natural erosion of oil sands caused slight to moderate impacts to the Athabasca River, but found "no evidence that industrial oil sands

operations were having an impact" (14). Tailings ponds leak pollutants into soil, groundwater and surface water (15, 6), but industry and the government suggest that quantities are insignificant (6), despite recent reports that leakage rates are 11 million L/day (16).

The Regional Aquatic Monitoring Program (RAMP) has been responsible for studying the effects of oil sands mining on the Athabasca River and its tributaries since 1997, and results have consistently suggested that impacts on water quality are negligible to low, or within regional baseline conditions (e.g., ref. 1). The 2008 RAMP community update, based on 2006 RAMP data, stated that "there were no detectable regional changes in aquatic resources related to oil sands development... only localized, site specific exceptions" (17). The only potential anthropogenic effect on water quality noted within the Athabasca River, its delta, or tributaries followed an approved diversion of the Tar River (17).

The RAMP is industry-funded and includes representatives of industry, government, local and aboriginal communities and environmental organizations. The program was highly criticized by a peer review of the program's five year report (1997–2001), which described the number of monitoring sites as inadequate, identified sampling practices that could ultimately neither measure nor detect impacts and stated that the program design could not assess cumulative impacts on water quality (18). The reviewers also "felt there was a serious problem related to scientific leadership, that individual components of the plan seemed to be designed, operated and analyzed independent of other components, that there was no overall regional plan, that clear questions were not addressed in the monitoring and that there were significant shortfalls with respect to statistical design of the individual components." Elsewhere, "the problems with the report are found in lack of details of methods, failure to describe rationales for program changes, examples of inappropriate statistical analysis, and unsupported conclusions" (18). The review was never made public, and RAMP raw data are considered to be proprietary and are not readily available for further analysis and critical review.

The Nunee Health Authority contracted a review of available data from 1997 to 2006, which also criticized the RAMP for inconsistent monitoring, weak data analyses, including bias, errors and overly conservative interpretations. The review noted a paucity of monitoring data near Fort Chipewyan and western Lake Athabasca (3). For these reasons, aboriginal and environmental groups have become increasingly critical of RAMP (6), and some have resigned from the program.

Timoney also concluded that the "people and biota of the Athabasca River Delta and western Lake Athabasca are exposed to higher levels of some contaminants than those upstream" (6). Of primary concern were arsenic, mercury, and PAHs, which appeared to be increasing above already high background concentrations from 1997 to 2006. The report expressed concern for public health, because some medical literature associated chronic exposure to these contaminants with diseases prevalent in Fort Chipewyan (6). For example, elevated arsenic concentrations have been associated with cancers of the bile duct, liver, urinary tract, and skin as well as vascular diseases and Type 2 diabetes (6). Another analysis of Athabasca River water quality data from 1960 to 2007 revealed decreasing trends in stream flow and increasing turbidity, nutrients and concentrations of some metals at Old Fort within the Athabasca Delta, downstream of oil sands development (19). Anthropogenic disturbance within the catchment was identified as a possible source, but establishing causal links would require further study (19).

Recognizing the huge scale of oil sands mining, the extent of potential impacts, and uncertainties due to inadequate monitoring data, there have been many recommendations for further studies of the sources, transport, fate and effects of contaminants in the Athabasca system (e.g., refs. 3–6).

**Analytical and Statistical Method Details. GIS analyses.** Catchments for each site were created using a 50 m shuttle radar topography mission (20) digital model and catchment areas were calculated. Digital disturbance data were assessed for relevance and a change analysis of forest ecozones within Alberta (1991–2001) (21), Canada access (roads, mines, forest fragments and reservoirs buffered by 500 m) (22), and the extent of oil sands development in 2008 (23) were chosen for further analysis. Disturbance and geologic formation data (24) were extracted within the extent of each catchment and areas were calculated. This process allowed for calculation of the proportion of each catchment containing McMF, overall surface land disturbance (a relative index), and land disturbance attributable to oil sands mining in 2008. The Firebag River catchment extends outside of Alberta into Saskatchewan where no comparable disturbance and geology data were available, thus, our analysis only included the Alberta portion of the Firebag River. For the same reason, catchments for Athabasca River sites do not contain tributaries that originate in Saskatchewan.

**PAC analyses.** Filters were dried by desiccator and weighed, and 0.1 g of oil sands sample was added to a 100 mL centrifuge tube. Each PMD, filter and oil sands sample was spiked with d8-Naphthalene, d10-Acenaphthene, d10-Phenanthrene, d12-Chrysene, and d12-Perylene and extracted with 100 mL 80:20 (v:v) pentane:dichloromethane in an ultrasonic bath. The extract was transferred to a 100 mL round bottom flask, evaporated to approximately 8 mL with a rotary evaporator and transferred to a 10 mL K-D contractor tube. The extract was concentrated to 1 mL under a stream of nitrogen and loaded onto a 1 cm ID column packed with 2 g of activated silica gel (100–200 mesh) at 130 °C. The column was eluted with 8 mL of pentane to obtain the alkane fraction and with 2 mL 80:20 (v:v) pentane:dichloromethane and 8 mL 50:50 (v:v) pentane:dichloromethane to collect the PAH fraction, which was concentrated under nitrogen and re-constituted in 1 mL of hexane. Snow extracts were filtered through 50 grams of sodium sulphate, concentrated as above and re-constituted with 1 mL of hexane. An internal standard of 50  $\mu$ L of 2-fluorobiphenyl was added to all extracts for chromatograph with a mass selective detector (GC-MSD) analysis. For each extract, 1.0  $\mu$ L was injected in splitless mode at 320 °C for separation on a 30 m, 0.25 mm ID, 0.5  $\mu$ m film DB-5MS fused silica capillary column (J&W Scientific, Folsom, CA). The initial oven temperature was 60 °C for 2 minutes which increased by 8 °C/min to 300 °C for 10 minutes and the flow rate of Helium as the carrier gas was 1.0 mL/min. The PAH were detected by selected ion monitoring (SIM) after ionization by a 70eV impact source.

**QA/QC.** Some of the deployed polyethylene membrane devices (PMDs) were lost or vandalized (winter: MU2, AR15 top and bottom, summer: ST3 and FR3, AR2 top and bottom). To be conservative and not overestimate PAC concentrations, values below method detection limits (Table S1) were not increased to the method detection limit for analyses. Several samples were contaminated by diesel oil, as indicated by PAC distributions limited to two- and three-ring homologues and were not included in analyses (winter: EL3, AR14, summer: AR17up, MU3 dup, HOR3 top, TR2, EL2, FR1, AR18, AR12, concentration range: 0.010 to 0.232  $\mu$ g/L). This contamination likely arises from brief exposure to high diesel concentrations caused by ephemeral spills from boating activity, pipeline, or storage tank leaks, fuel transfers, unreported spills, etc. Comparable instances of such contamination were evident in a similar study of background PAC in Prince William

Sound, Alaska in 2004 (20). In summer, the relative percent difference was <19.8% for duplicates from impacted and reference sites. Dissolved PAC concentrations in trip (winter: 0.055, summer: 0.036  $\mu$ g/L) and field (winter:  $0.050 \pm 0.019$ , summer:  $0.050 \pm 0.009$ ) blanks were low in both seasons. In summer, field blanks deployed at impacted sites contained more dissolved PAC than those from reference sites, indicating that PMDs collected dissolved PAC from the air. Dissolved PAC concentrations in PMDs deployed at upstream and some midstream sites were lower than field and trip blanks, indicating that ambient stream concentrations were so low that PAC initially present in the deployed PMDs leached into the sampled water stream, a phenomenon observed elsewhere (25).

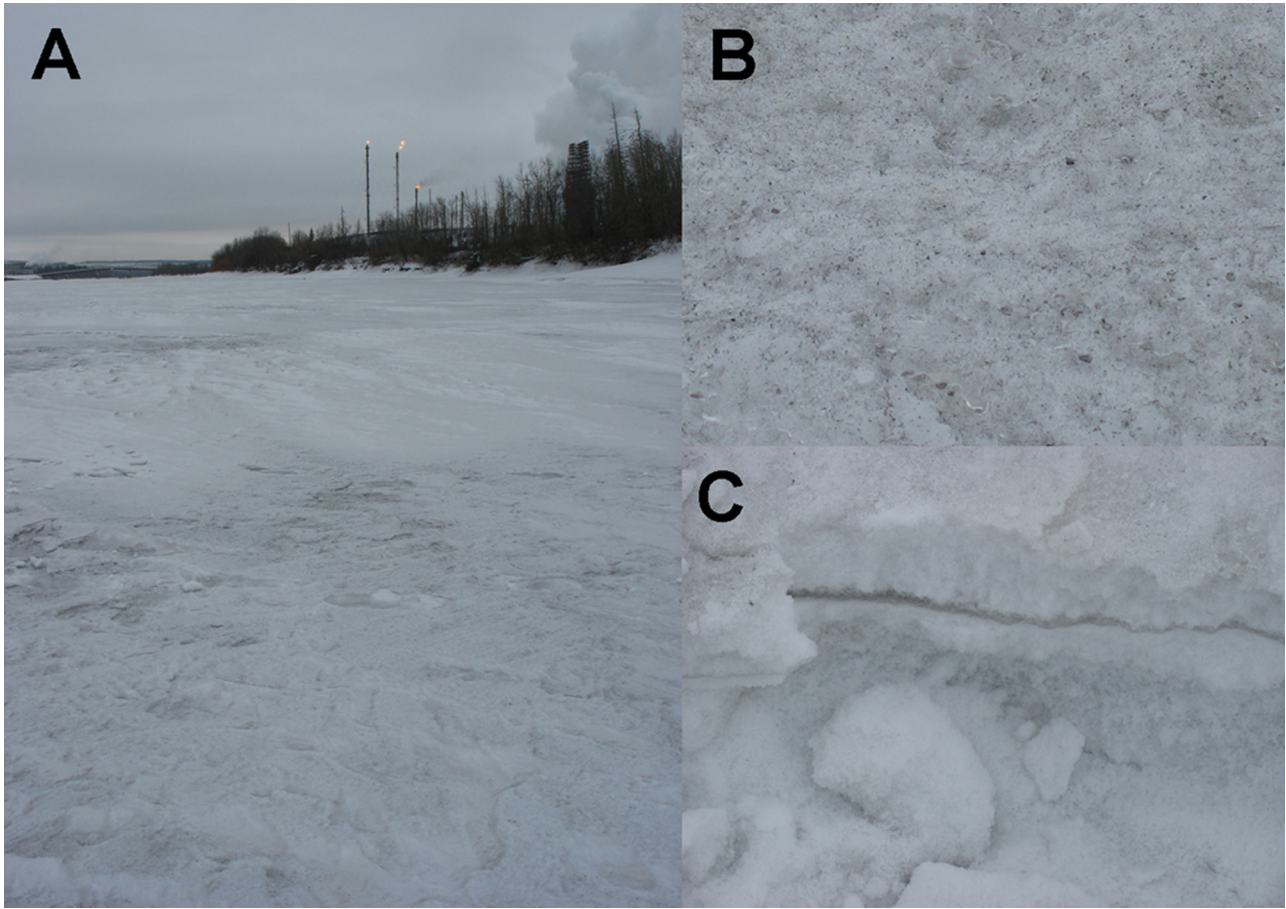
**PAC source identification.** Analysis of four samples of oil sands collected from the east ( $n = 2$ , ST3, east bank of the Athabasca River) and west ( $n = 2$ , Syncrude and west bank of the Athabasca River) sides of the Athabasca River contained PAC ranging from 64.9 to 282.5  $\mu$ g/g. Four homologue groups accounted for most of the PAC: dibenzothiophenes (28–42%), phenanthrenes/anthracenes (10–30%), fluoranthenes/pyrenes (13–28%), and benzantracenes/chrysenes (9–21%). Ratios of ( $\Sigma$ -dibenzothiophenes):( $\Sigma$ -phenanthrenes/anthracenes, or  $\Sigma$ D: $\Sigma$ P) >0.8 and ( $\Sigma$ -benzantracenes/chrysenes):( $\Sigma$ -phenanthrenes/anthracenes, or  $\Sigma$ C: $\Sigma$ P) >0.065 were used as indicators of an oil sands source in the PMD samples, with the low value of the second ratio reflecting the much lower solubility of benzantracenes/chrysenes compared with phenanthrenes/anthracenes (dibenzothiophenes are somewhat more soluble than phenanthrenes/anthracenes) (26). We considered PMD samples with both ratios lower than these values as contaminated with diesel oil, because dibenzothiophenes and benzantracenes/chrysenes are mostly removed from diesel oil by sulfur removal and distillation, respectively. These criteria were only applied to PMD samples that contained at least 100 ng of PAC in the aliquot extracted to avoid misinterpretations due to benzantracenes/chrysenes below detection limits.

**Ratio of PAC to bitumen.** The four oil sands samples analyzed for PAC (see *PAC source identification*) were also analyzed for percent organic extractable at the University of Alberta. Oil sands samples were weighed before and after extraction with dichloromethane. The percent organic extractable of the four oil sands samples ranged from 11.3 to 16.9%, with a mean of 14.7%. PAC concentrations and percent organic extractable of the four samples were used to calculate the PAC to bitumen ratio of  $0.000649 \pm 0.000168$ . The four oil sands samples may not be completely representative of what is mined and processed, but were what was accessible. This ratio should be relatively insensitive to change from volatility losses. As shown in Fig. S4.4, the relative abundances of the more volatile PAC such as the naphthalenes and the parent and methyl-substituted three-ring PAC are small compared with the more substituted fluorenes, dibenzothiophenes, phenanthrenes/anthracenes, fluoranthenes/pyrenes and benzantracenes/chrysenes. Furthermore, to the extent that volatility losses of PAC exceed those of the remaining non PAC material in the bitumen, oil deposition would be underestimated.

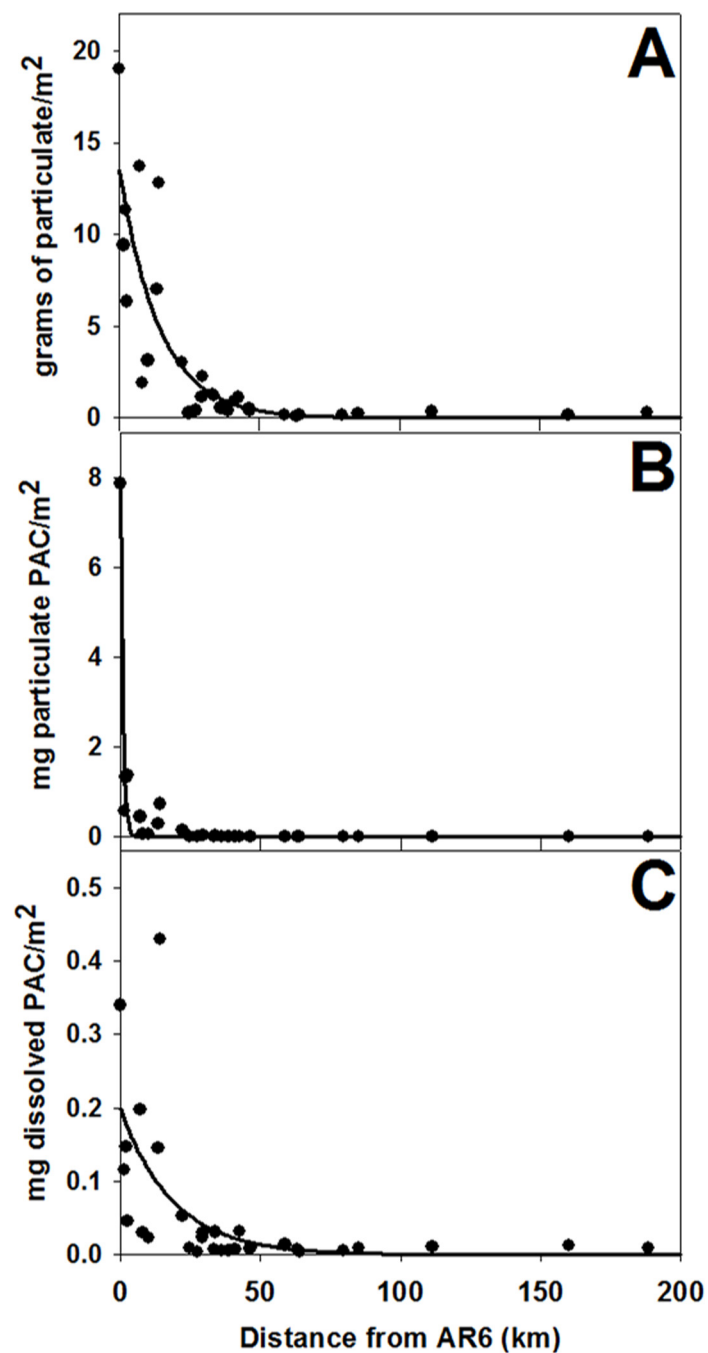
**Estimation of aqueous PAC concentrations.** PMD results were presented as estimated aqueous PAC concentrations, based on the assumption of equilibrium between the two phases. Sampling rates of PAH by semipermeable membrane devices (SPMDs) and PMDs are indistinguishable (27, 28), but PMDs reach equilibrium with ambient conditions more quickly because their absorptive capacity is only  $\approx 20\%$  that of SPMDs per unit mass (27, 29). Naphthalenes reach equilibrium with SPMDs in about 10 days, but >30 days are required for three- and four-ring PAH (29). We used the equilibrium assumption because of the faster approach to equilibrium with PMDs and because the aqueous concentrations calculated on this assumption are underestimates to the extent that equilibrium was not attained. The approach to equilibrium is sensitive to flow across the PMD surface and to the extent of biofouling, so we cannot be sure our PMDs reached equilibrium with all of the ambient PAC



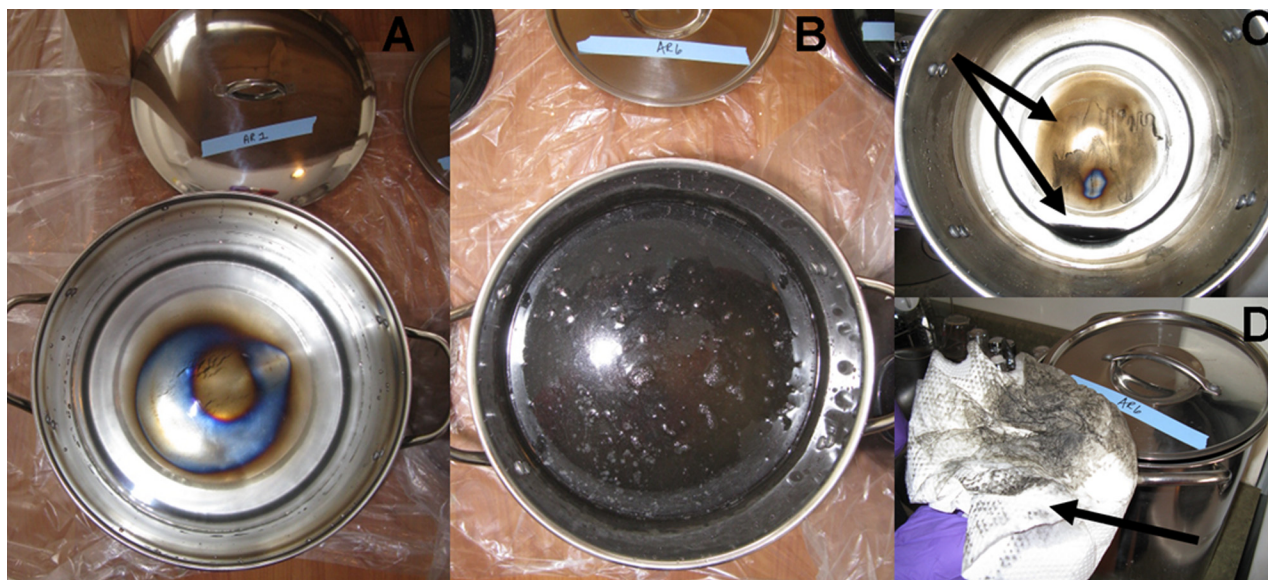




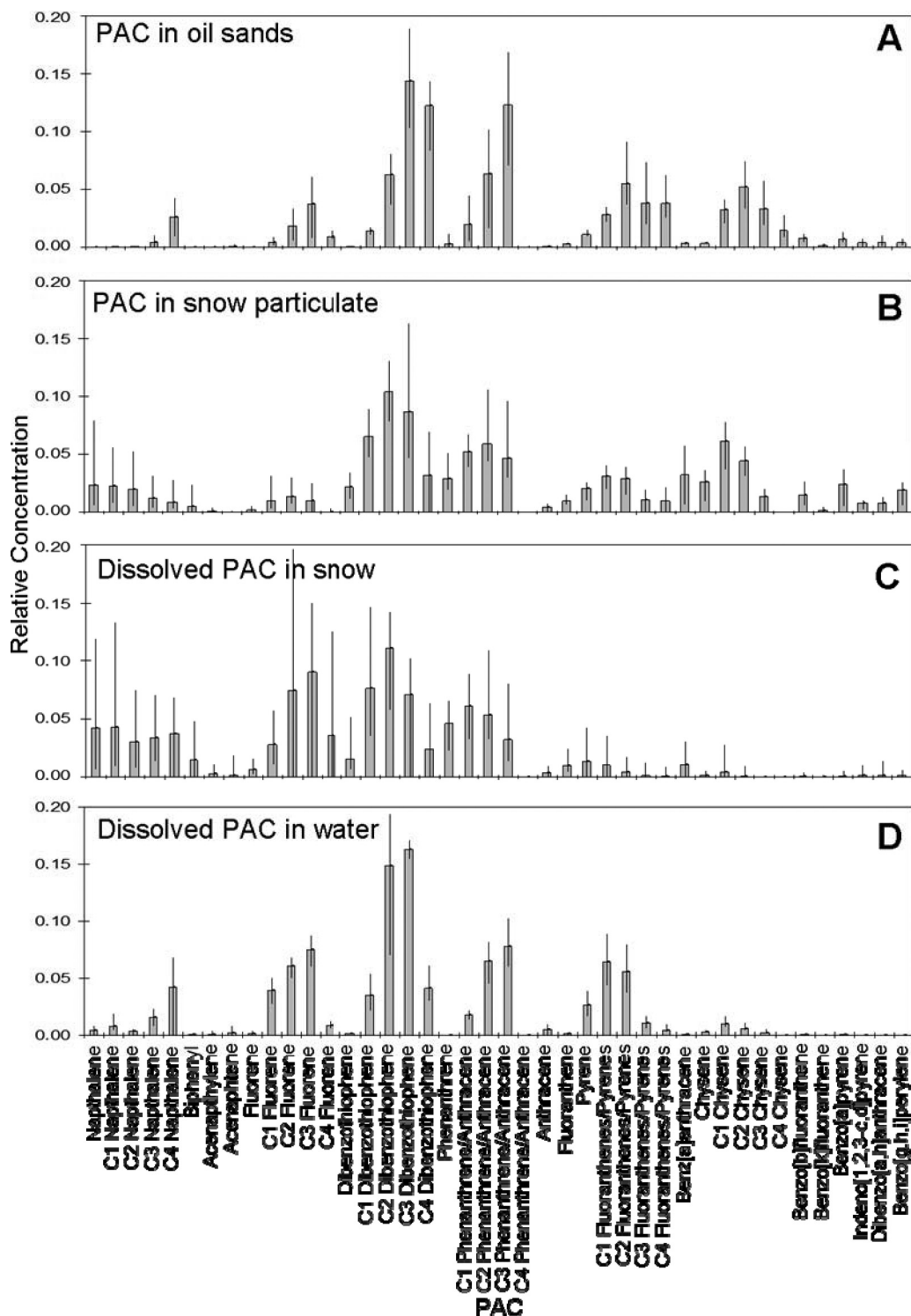
**Fig. S1.** Site AR6 photographed 26 February 2008. (A) Dirty snow on the Athabasca River (facing south). (B) close-up of surface snow at AR6. (C) Snowpack at AR6. Photographs courtesy of E.N.K.



**Fig. S2.** Accumulation of particulate (A), particulate PAC (B), and dissolved PAC (C) in the snowpack as a negative exponential of distance from AR6 (near Syncrude and Suncor upgrader facilities).

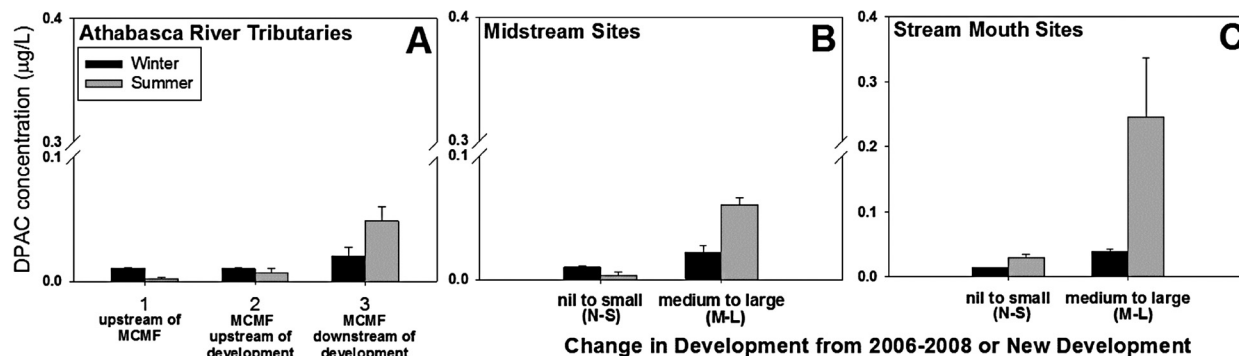


**Fig. S3.** Melted snow in pots from sites AR1 (unimpacted) (A) and AR6 (near Syncrude and Suncor upgrader facilities) (B, C, and D). Note oil in melted snow from AR6 in B. Oil and dark particulates are noticeable at the bottom of the pot after draining the sample in C. The originally white paper towel used to wipe out the pot is visible in D. Photographs courtesy of E.N.K.



**Fig. S4.** Relative concentration of PAC in oil sands (includes oil sand from Syncrude, Steepbank stream mouth, east, and west bank of the Athabasca River) (A), dissolved PAC in snow (B), PAC in snow particulate (includes snow sites AR2, AR16, AR4, AR6, AR7, AR8, BE2, BE3, EL2, EL3, MU1, MU2, MU3, ST1, ST2, ST3, TR2, TR3) (C), and dissolved PAC in water (includes contaminated sites MCC, MACK, CALR, FOR, and EL3 sampled during the summer) (D). Gray vertical bars indicate averages, black bars are ranges.





**Fig. S5.** Estimated dissolved PAC concentrations ( $\mu\text{g/L}$ ) during winter (W) and summer (S). (A) The Athabasca River tributaries [ $n = 3$  for 1, 2, and 3 (W&S)]. (B) Midstream tributary sites [nil to small:  $n = 2\text{W}, 2\text{S}$ ], medium to large:  $n = 3\text{W}, 2\text{S}$ ]. (C) Stream mouth sites [nil to small:  $n = 4$  (W)  $n = 6$  (S), medium to large:  $n = 2$  (W),  $n = 6$  (S)]. (D) the Athabasca River, Athabasca Delta and Lake Athabasca (W&S). \*, indicates samples contaminated by diesel fuel. No tributary sites contaminated by diesel fuel were included in figures. McMF, McMurray Formation. Error bars are standard error of the mean. (A) PAC concentrations differed significantly among sites (two-way ANOVA, In transformation,  $P = 0.006$ ,  $\beta = 0.87$ ), but not season ( $P = 0.228$ ,  $\beta = 0.107$ ). The greater apparent trend of increasing PAC downstream in summer compared with winter was nearly significant (interaction  $P = 0.057$ ) with only moderate power to detect actual differences with this test ( $\beta = 0.433$ ). Post hoc testing revealed that PAC concentrations in upstream and midstream sites were not significantly different ( $P = 0.568$ ), but were significantly lower than at stream mouth sites ( $P < 0.009$ ). (B) At midstream sites, disturbance effects and the interaction of season and disturbance were significant (two-way ANOVA, In transformation, disturbance:  $P = 0.006$ ,  $\beta = 0.946$ , interaction:  $P = 0.035$ ,  $\beta = 0.583$ ). However the seasonal effect was not significant, but the power of the test was low, likely because of small sample size ( $P = 0.717$ ,  $\beta = 0.050$ ). Post hoc testing revealed that winter and summer PAC concentrations were greater at sites with M-L development, than sites with N-S development (W:  $P = 0.006$ , S:  $P = 0.004$ ). (C) At stream mouth sites, both seasonal and disturbance effects were highly significant (two-way ANOVA, In transformation,  $P < 0.001$ ,  $\beta > 0.976$ ), however, the interaction of season and disturbance was not significant ( $P = 0.133$ ,  $\beta = 0.201$ ). Post hoc testing revealed that winter and summer PAC concentrations were greater at sites with M-L development, than sites with N-S development (W:  $P = 0.041$ , S:  $P < 0.001$ ).





**Fig. S6.** New industrial development along the eastern bank of the Athabasca River,  $\approx 8$  km upstream of AR15, on August 12, 2008. Photograph courtesy of E.N.K.



**Fig. S7.** "Winter haze" and erosion of "dust" from oil sands mining activity on February 26, 2008. Photograph courtesy of Dr. Kevin Timoney.

Target analyte	Instrument detection limit, µg/L	Method detection limit for snow, ng/L*	Method detection limit for PMD, ng/g of strip†	Method detection limit for oil sand, ng/g
Naphthalene	0.42	0.05	0.36	4.16
C1 naphthalene	0.42	0.05	0.36	4.16
C2 naphthalene	0.42	0.05	0.36	4.16
C3 naphthalene	0.42	0.05	0.36	4.16
C4 naphthalene	0.42	0.05	0.36	4.16
Biphenyl	0.21	0.03	0.18	2.13
Acenaphthylene	0.19	0.02	0.17	1.93
Acenaphthene	0.71	0.09	0.61	7.10
Fluorene	0.53	0.07	0.45	5.26
C1 fluorene	0.53	0.07	0.45	5.26
C2 fluorene	0.53	0.07	0.45	5.26
C3 fluorene	0.53	0.07	0.45	5.26
C4 fluorene	0.53	0.07	0.45	5.26
Dibenzothiophene	0.30	0.04	0.26	2.97
C1 dibenzothiophene	0.30	0.04	0.26	2.97
C2 dibenzothiophene	0.30	0.04	0.26	2.97
C3 dibenzothiophene	0.30	0.04	0.26	2.97
C4 dibenzothiophene	0.30	0.04	0.26	2.97
Phenanthrene	0.22	0.03	0.19	2.20
C1 phenanthrene/anthracene	0.22	0.03	0.19	2.20
C2 phenanthrene/anthracene	0.22	0.03	0.19	2.20
C3 phenanthrene/anthracene	0.22	0.03	0.19	2.20
C4 phenanthrene/anthracene	0.22	0.03	0.19	2.20
Anthracene	0.38	0.05	0.32	3.77
Fluoranthene	0.26	0.03	0.22	2.59
Pyrene	0.32	0.04	0.27	3.17
C1 fluoranthenes/pyrenes	0.32	0.04	0.27	3.17
C2 fluoranthenes/pyrenes	0.32	0.04	0.27	3.17
C3 fluoranthenes/pyrenes	0.32	0.04	0.27	3.17
C4 fluoranthenes/pyrenes	0.32	0.04	0.27	3.17
Benzanthracene	0.63	0.08	0.54	6.27
Chrysene	0.66	0.08	0.57	6.59
C1 chrysene	0.66	0.08	0.57	6.59
C2 chrysene	0.66	0.08	0.57	6.59
C3 chrysene	0.66	0.08	0.57	6.59
C4 chrysene	0.66	0.08	0.57	6.59
<b>Benzo<b>fluoranthene</b></b>	0.47	0.06	0.40	4.69
Benzo[k]fluoranthene	0.74	0.09	0.63	7.35
Benzo[a]pyrene	0.74	0.09	0.64	7.40
Indeno[1,2,3-c,d]pyrene	1.30	0.16	1.12	13.03
Dibenzo[a,h]anthracene	0.37	0.05	0.32	3.73
Benzo[g,h,i]perylene	0.64	0.08	0.55	6.40

\*Snow MDL was calculated based on the extraction of 4 L of snow.

<sup>†</sup>The PMD MDL was calculated based on the mean weight of 1/2 a polyethylene strip.